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CORROSION OF STAINLESS STEELS IN HIGH TEMPERATURE WATER AND STEAM

by

M. WARZEE*, W.R. RUSTON*, P. de DORLODOT*,
J. HENNAUT*and J.-Ph. BERGE **

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SUMMARY

The corrosion of stainless steels in steam increases regularly between 200 and 300° C. This is not so in water: there, corrosion as function of temperature shows a marked maximum around 250° C for AISI 410 steel. For AISI 304 steel the maximum, which was not actually observed, must lie at a lower temperature. The quantity of dissolved metal is responsible for the maximum. It was shown that magnetite crystals grow out of the solution and that this redeposition may cause underestimation of corrosion values obtained in static autoclave tests. The observed phenomenon is of great technical significance because the cristallisation of magnetite from solution may cause mass transfer from cooler to hotter parts in nuclear reactors cooled with water and operating around 300° C.

CONTENTS

Corrosion of Stainless Steels in High Temperature Water and Steam(*)

INTRODUCTION

In many steam generators, particularly in nuclear power plants with boiling water reactors, the structural materials, generally stainless steels, are in contact with pressurised water at high temperature and with steam. It has been observed in the laboratory that marked differences in corrosion behavior appear when the stainless steels are exposed either to water, to wet steam or to superheated steam.

Among the factors which may influence the corrosion resistance towards water or steam in the one or the other way, the surface preparation of the specimens was found to be of considerable importance. These observations have been published elsewhere [1 to 5] and only the principal results are repeated here:

— In pressurised water, between 200 and 300° C, AISI 304 steels having undergone a mechanical surface treatment (f.i. milling) corrode very much quicker than the same steels from which the cold worked surface layers were removed by electrolytic polishing prior to the test.

  The corrosion rates at 300° C, measured by the so-called "hydrogen diffusion" method (**) are 0.003 $mg.dm^{-2}.hr^{-1}$ for electrolytically polished specimens, and 0.008 $mg.dm^{-2}.hr^{-1}$ for milled specimens respectively after 1000 hours.

  This effect is much less marked for ferritic steel AISI 410 at 200° C and 250° C and it disappears in water at 300° C and 350° C.

— In superheated steam, surface treatments producing cold work do not affect the corrosion of AISI 304 and 410 steels between 200 and 300° C. However, at 400° C and still higher temperatures the beneficial effects of surface cold work are considerable. The explanation of these phenomena has already been published elsewhere [5-8].

The present paper deals with the comparison of the corrosion rates of stainless steels with identical surface treatments in water and in superheated steam at different temperatures.

(*) Manuscript received on February 9, 1966.
(**) First described by M.C. Bloom and al. [6-7].

EXPERIMENTAL

The results obtained with two types of stainless steel only are discussed here; the compositions of the specimens are shown by the following table:

Steel	Origin and trade mark	C	Si	S	P	Mn	Cr	Ni
AISI 304	KRUPP V2A-Supra IIa	0.04	0.50			1.1	18.8	11.0
AISI 410	KRUPP V13F IIa	0.07	0.32	0.006	0.021	0.38	13.4	—

The specimens are electrolytically polished in an aceto-perchloric acid bath and then rinsed with boiling water. The corrosion tests are carried out in autoclaves of 250 ml, each of which may contain 16 specimens (100 × 10 × 1 mm). The water used for filling the autoclaves is of very high purity; its measured resistivity is 20 MΩ.cm and its oxygen content is below 15.10^{-3} ppm. The evaluation of corrosion is carried out by weighing with a precision of 10^{-5} g.

For correct evaluation of the total corrosion, the metal present in adherent oxides, as well as the metal in the water must be accounted for. To achieve this, the corroded specimens are exposed to hydrogen at 800° C [7] in order to reduce the adherent oxides to metal. The hydrogen used comes from a purifier with palladium membranes; its residual impurity content is less than 1 vpm. The reduction treatment of about 4 hours duration, when applied to electrolytically polished reference specimens, produces a weight loss of less than 3.10^{-5} g.

This method allows the direct determination of the quantity of metal contained in the non-adherent oxides and of the oxygen fixed by corrosion. However, in order to establish from these values the total corrosion, it is necessary to make assumptions concerning the composition of the formed oxide. For the calculations the mass ratio metal/oxygen of magnetite was adopted. It was possible to show in the case of AISI 304 steels that the error introduced by this assumption was negligible. As a matter of fact, with these steels, it is possible to achieve a quantitative descaling of adherent oxides [9]. The treatment consists in boiling for 1 1/2 hours in a solution containing 20 % NaOH and 3 % $KMnO_4$; the oxide layer is then easily removed by wiping with a nylon cloth. The results obtained by this process very closely agree to those obtained after reduction under hydrogen.

It must be noted that the two methods of evaluation of the corrosion of stainless steels, allow to determine exactly the total corrosion of the specimens, even if products coming from other sources were deposited on their surface. It is however evident that in such a case no precise figures could be obtained for the respective quantities of the two components of total corrosion products from a given specimen.

RESULTS AND DISCUSSION

1. The values of total corrosion of AISI 410 and AISI 304 steels, after 1000 hours autoclaving, are shown by figures 1 and 2.

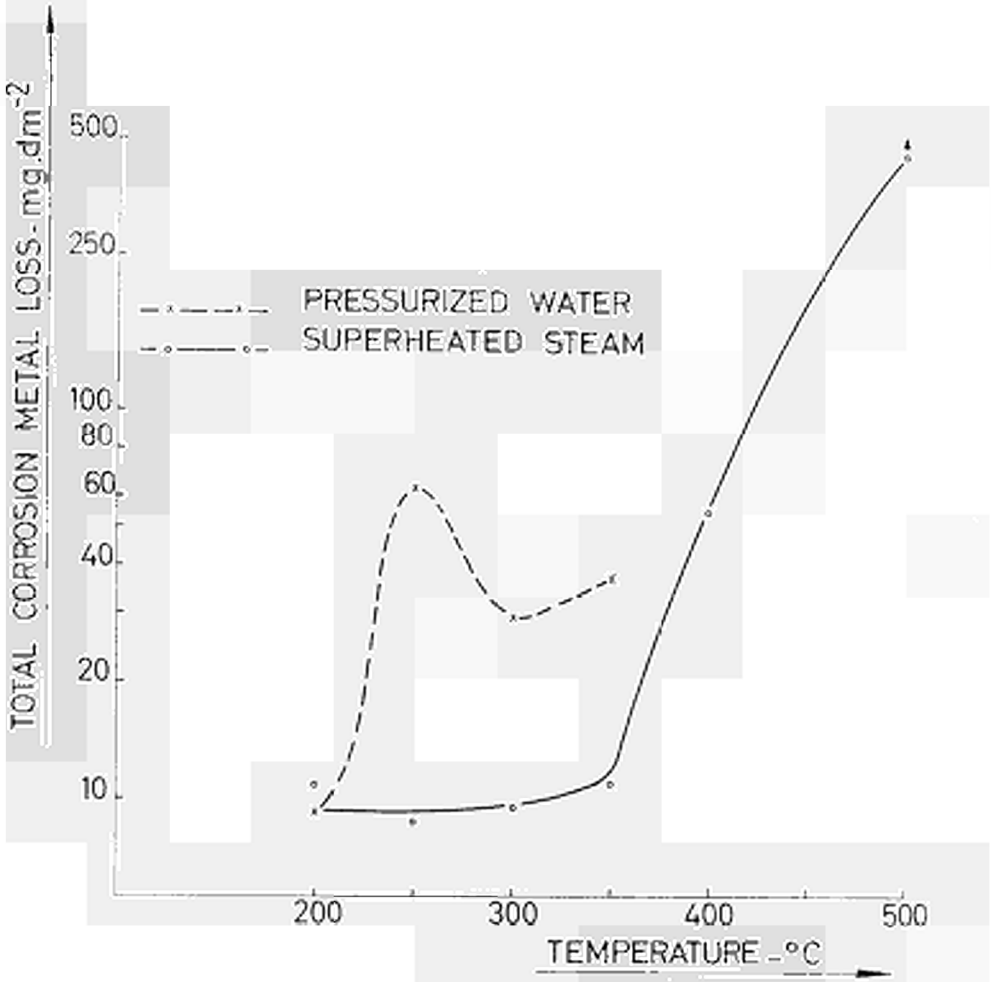

Figure 1

Total corrosion of type 410 stainless steel after 1000 hours' exposure in autoclave.

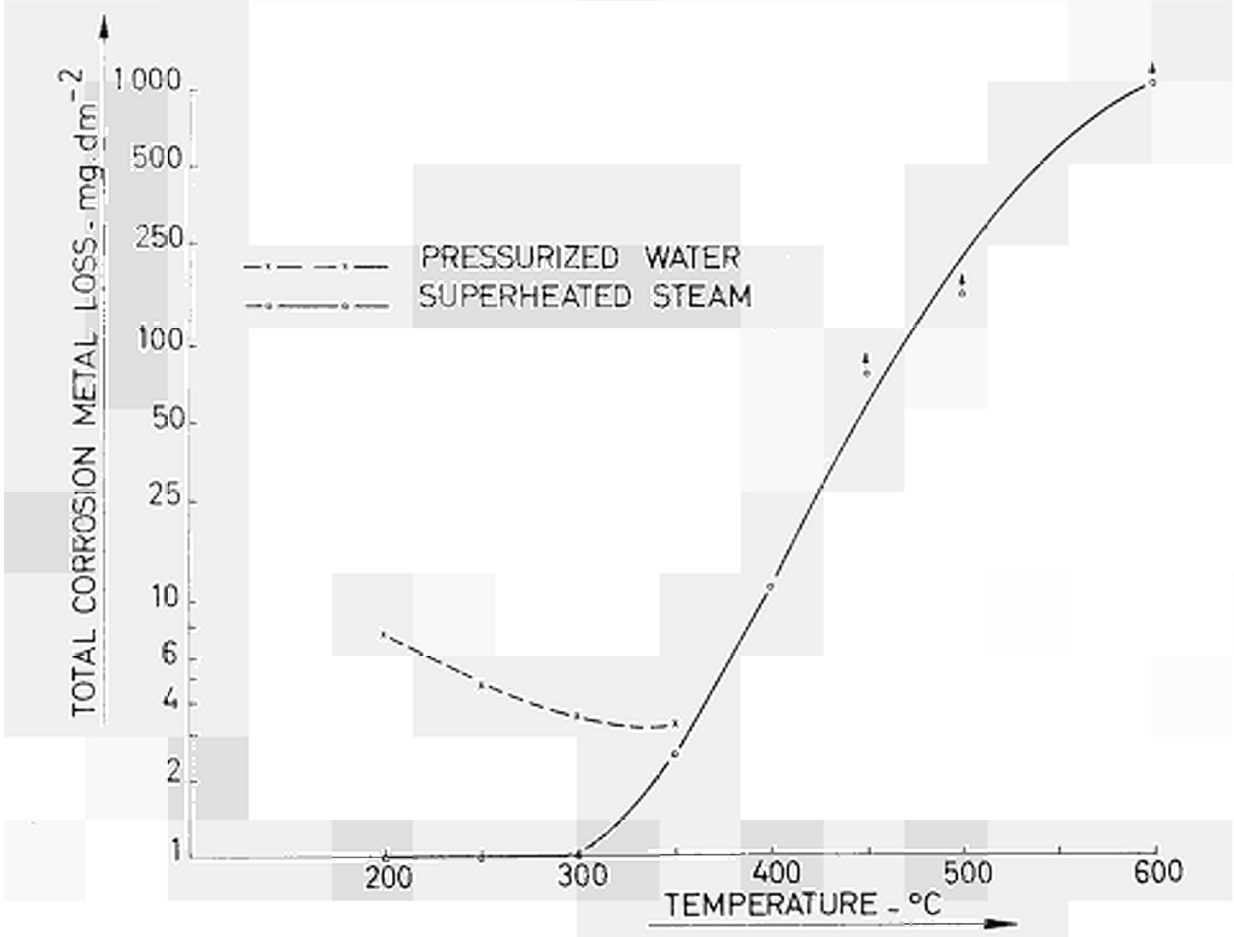

Figure 2

Total corrosion of type 304 stainless steel after 1000 hours' exposure in autoclave.

For AISI 410 steel, the corrosion in steam increases steadily between 200° C and 400° C. In water, however, a very marked maximum of total corrosion was observed in the test at 250° C. The AISI 304 steel corrodes very much less in water as well as in steam. Nevertheless, the observed total corrosion in water is significantly higher at 200° C than at 300° C.

In superheated steam the quantity of lost metal is extremely low for both steels. From the curves of figure 3 it becomes however apparent that the high value of total corrosion and the maximum observed at 250° C for AISI 410 steel are accompanied by an important quantity of metal lost into the autoclave.

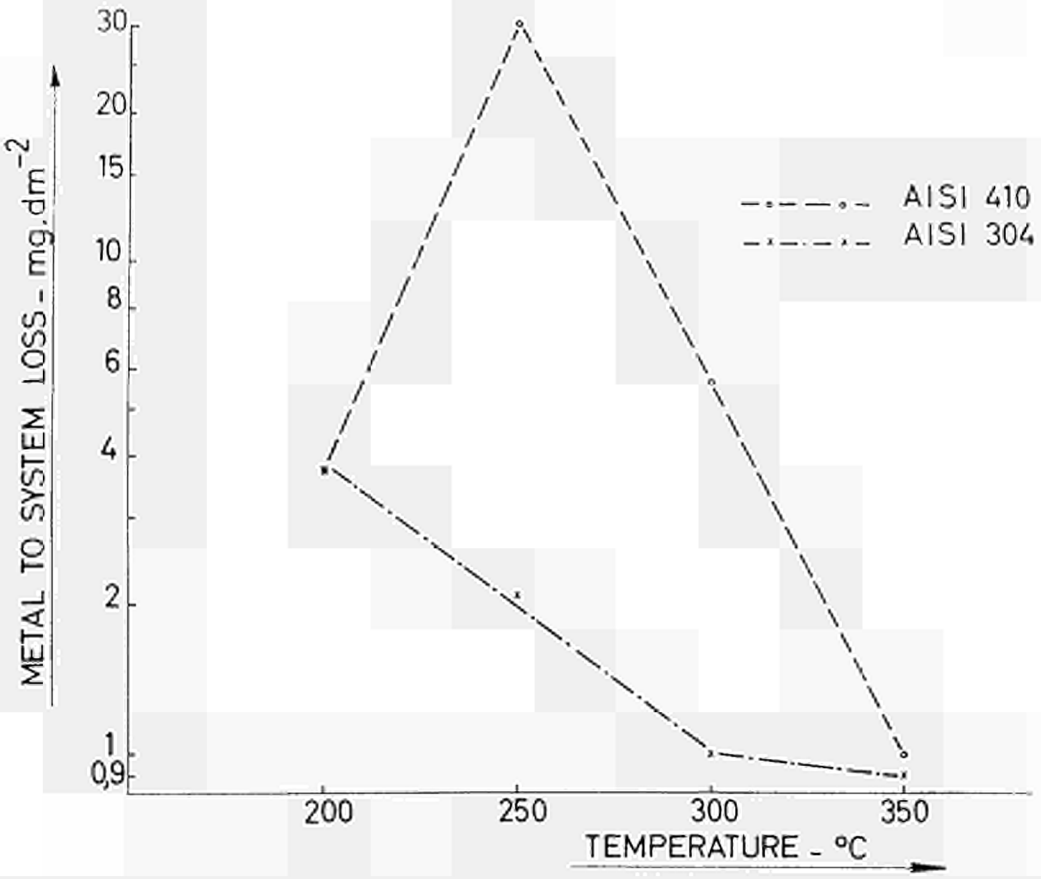

Figure 3

Metal to system loss of types 410 and 304 stainless steel after 1000 hours' exposure to high temperature water.

2. The analysis of the non adherent corrosion products was carried out for AISI 410 steel after tests at three different temperatures: 200° C, 250° C and 300° C. For this purpose a platinum crucible was placed in the autoclave in order to avoid pollution of the water by products coming from the walls of the autoclave and to make possible the quantitative recovery of the non adherent corrosion products.

The platinum crucible is filled with 15 ml of water and wires of AISI 410 steel (total surface: 0.8 dm^2) are placed into it. The autoclave itself also contains a certain

quantity of water into which plunges the crucible; this avoids evaporation of the water from the crucible which might condense on the cooler parts of the autoclave [10].

After experiments of short duration (75 hours) the water and the precipitated corrosion products contained in the crucible are analysed. The chemical analysis shows that chromium is absent. The following iron contents were found:

Test temperature °C	200	250	300
Iron content in µg	110	545	307

One sees that the quantities of metal lost into the water at different temperatures show the same trend as the corrosion values at these same temperatures.

These results complete and confirm those of M.E. Jones [11] who studied inconel type alloys in ammonia containing water between pH 8.5 and pH 10.5. Jones investigated the solubility of the corrosion products of the different alloy constituents of inconel and he could show that the solubility of the corrosion products of iron passes through a maximum, while that of nickel corrosion products steadily decreases between 24° C and 340° C. In the absence of oxygen chromium was found to be practically insoluble. For the inconel, Jones found the maximum solubility of iron corrosion products around 177° C.

In the case of AISI 304 steel, the solubility maximum was not detected because the lowest temperature in the present tests was 200° C. While the position of the maximum cannot be given, its existence is nevertheless proved by the shape of the curve of total corrosion in water between 200 and 300° C. In case of AISI 410 steel the maximum found in demineralised water is located at higher temperature values than that obtained by Jones for inconel in alkaline water.

Several intermediate steps are suggested in literature for the production of magnetite from steel by oxidation in water [12, 13, 14].

$$Fe + 2\,H_2O \rightarrow Fe(OH)_2 + H_2$$

This ferrous hydroxide has a very high solubility product with respect to other iron oxides.

$$Fe(OH)_2 \rightleftarrows Fe^{2+} + 2\,OH^-$$

$$S = |Fe^{2+}|\ \ |OH^-|^2$$

The values found by different authors vary between 10^{-14} and 10^{-16} [15 to 18].

Ferrous hydroxide changes into magnetite (Shikorr reaction) [19].

$$3\,Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + H_2O$$

This reaction becomes very fast when temperature increases [18, 20, 21].

The existence of a solubility maximum may hence be explained qualitatively by the fact that the rate of production of ferrous hydroxide from the iron increases with

increasing temperature, but that its rate of decomposition is also very much accelerated when the temperature rises from 150° C towards 300° C.

3. Micrographic examinations of the morphological features of the oxide films supply complementary informations on the observed phenomena. The oxide films obtained in steam at 250° C are very thin and homogeneous.

On specimens oxidized in water at 250 C and 300° C however, well developed crystals appear, the dimensions of which may attain several microns (Figure 4).

These crystals are in epitaxial relation to the base metal (Figure 5) and they appear on certain metal grains only (may be due to the favourable orientation of the

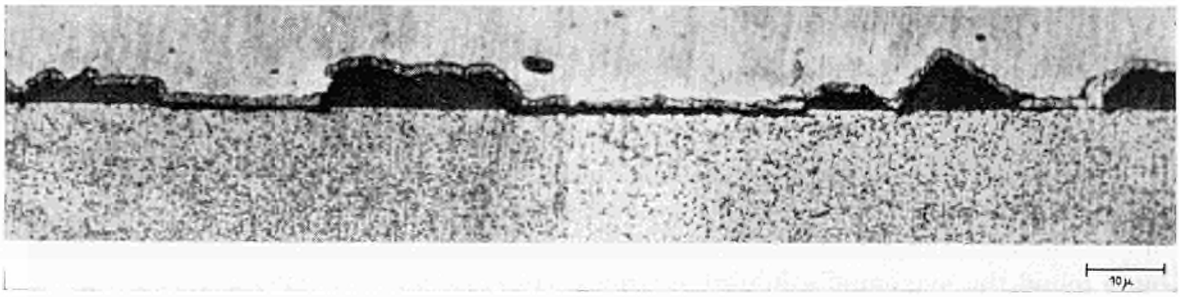

Figure 4

Oxide formed on type 410 stainless steel after 1000 hours' exposure to 250° C water. Cross-section view. With protective cobalt layer. Etchant: HNO_3-HF solution.

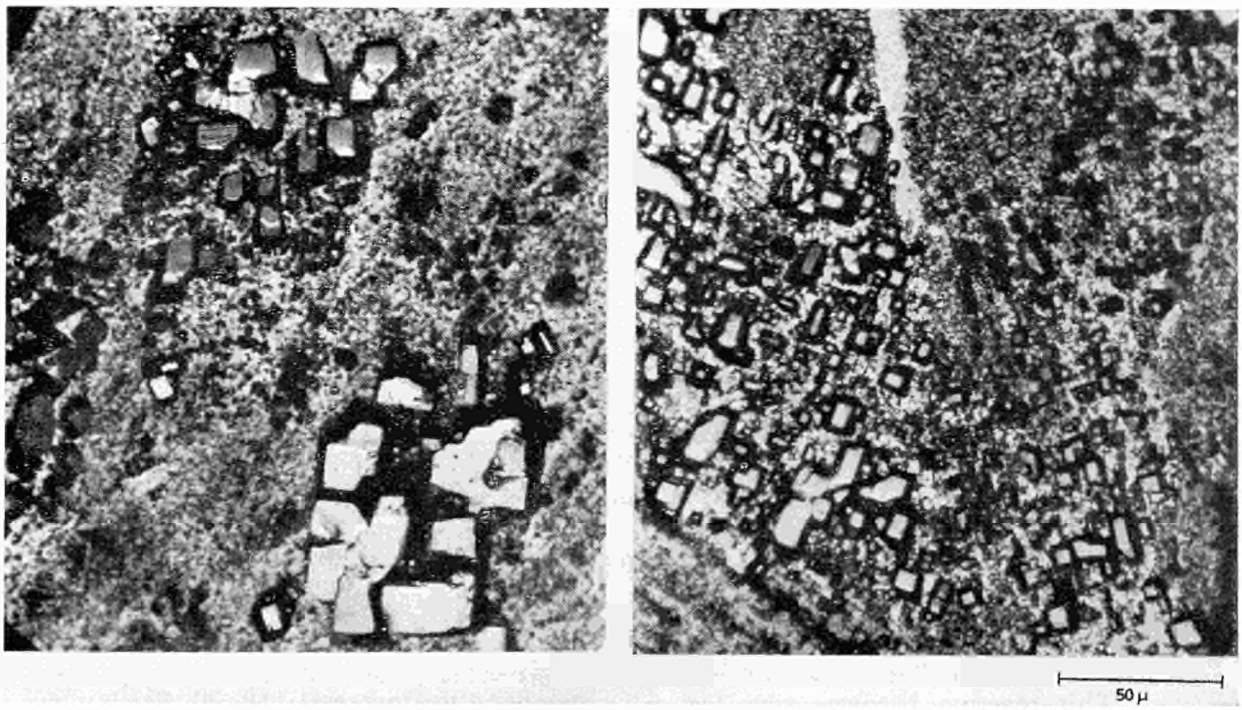

Figure 5

Oxide formed on type 410 stainless steel after 1000 hours' exposure to 250° C water. Surface view— Unetched.

latter). By X-ray diffraction, the crystals were identified as magnetite. These crystals show a different aspect than those formed at high temperature (400° C) in superheated steam (Figure 6).

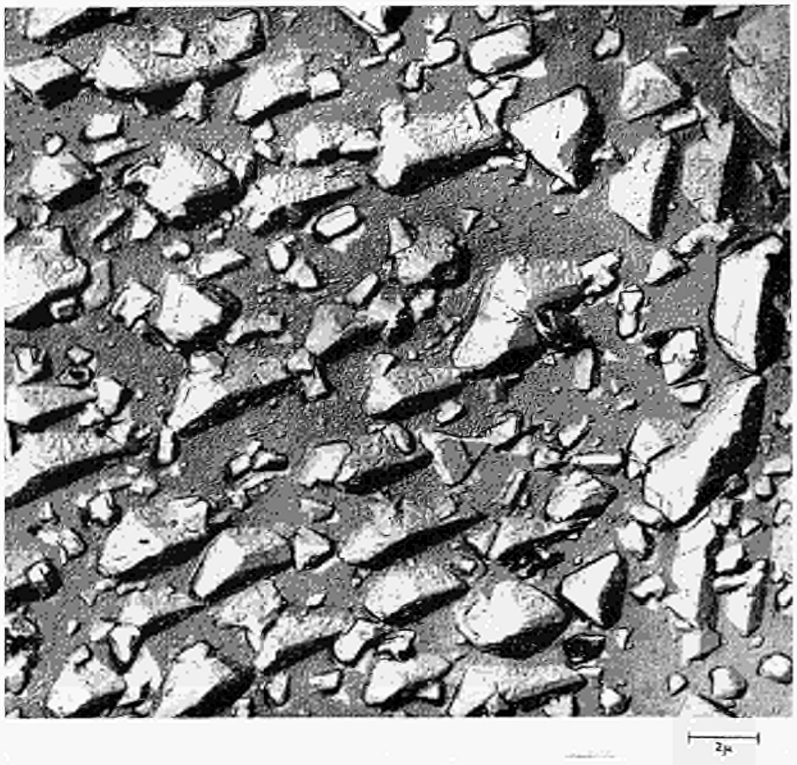

Figure 6

Oxide formed on type 304 stainless steel after 1000 hours' exposure to 400° C superheated steam—Unetched—Carbon replica.

In the latter case the crystals also epitaxially grown on the metal and consisting of magnetite, are no more localized on certain metal grains only, but appear on the entire surface of the polycrystalline specimen. At higher temperatures (500° C) they form a continuous layer of magnetite [22]. These morphological observations suggest that the mechanism of formation of magnetite crystals is without doubt, different when the oxidizing medium is either water between 200° and 300° C, or superheated steam at still higher temperature. It seems probable that the crystals formed on specimens oxidized in water (between 200 and 300° C) grew out of the ferrous hydroxide solution. In order to verify this hypothesis chromized platelets of AISI 304 steel were exposed to water at 250° C, together with specimens of AISI 410 steel. Normally, these chromized specimens develop a thin film of very protective chromium oxide. When they were treated in the same autoclave together with the AISI 410 specimens, they were locally covered by the same type of crystals that were observed on the AISI 410 specimens. After reduction under hydrogen at 800° C it was found that these specimens weighed more than their initial weight. This proves that the magnetite crystals found on the surface of these specimens were formed out of the liquid phase. This crystallization is probably caused or accelerated by differen-

ces in temperature within the autoclaves. As a matter of fact, the crystals have a tendency to appear on the regions of specimens located in the center of the autoclaves where the temperature and hence also the decomposition rate of the hydroxide are the highest.

We have shown elsewhere [22] that two processes contribute to the growth of the oxide in steam at 500° C: on the one hand anions migrate towards the metal, thus forming a spinel layer rich in chromium and nickel and in which a matrix of austenite with unit cell dimensions different from the original ones persists. On the other hand, cations (iron only) diffuse towards the surface, forming there a well crystallized layer of magnetite. This two-fold process is analogous to the growth mechanism of oxide on low carbon steel as it has been shown by Potter and Mann [23-24].

The micrograph of Fig. 4 shows that an analogous mechanism may be suggested for the oxidation in 250° C water. As a matter of fact, the magnetite crystals protect the metal from further oxidation and it can be seen that on other places the oxide penetrates into the interior. It thus appears that the continuous oxide layer is formed by diffusion of anions. The counter diffusion of iron through this layer and its oxidation at the oxide-water interface do not produce a continuous layer of magnetite, as it happens in steam at 500° C. The iron, instead, is oxidized to ferrous iron and solubilized, to a large extent at least. The large crystals of magnetite found on the surface of the specimens grow out of this solution of ferrous hydroxide.

CONCLUSIONS

The consequences of this solubilization and redeposition of the corrosion products may be experimentally and technically very significant. On the one hand, the evaluation of corrosion in static non purified systems calls for caution: the figures for the quantity of metal lost into the solution, obtained by weighing either using the hydrogen reduction method or after descaling, tend to be too low because part of the dissolved metal reprecipitates in the form of very adherent crystals. The figures for the total corrosion established by the one or the other method are however not modified by this deposition of magnetite, except in the case where deposition is very abundant which may protect a non negligible portion of the specimen surface from further corrosion.

On the other hand, the technical significance of the phenomenon becomes apparent from the mass transfer it is likely to produce in nuclear reactors cooled by water and operating around 300° C: there, corrosion products solubilized in the cooler parts of the circuit have the tendency to reprecipitate on the hotter fuel element cannings, seriously affecting thereby the heat transfer properties of the latter (fouling).

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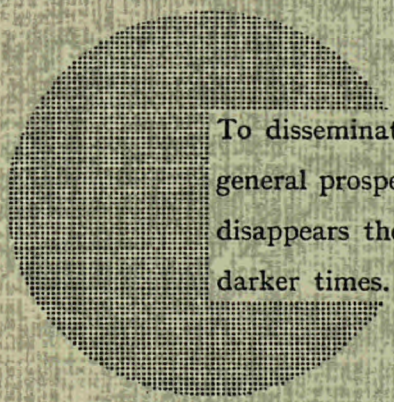

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Alfred Nobel

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